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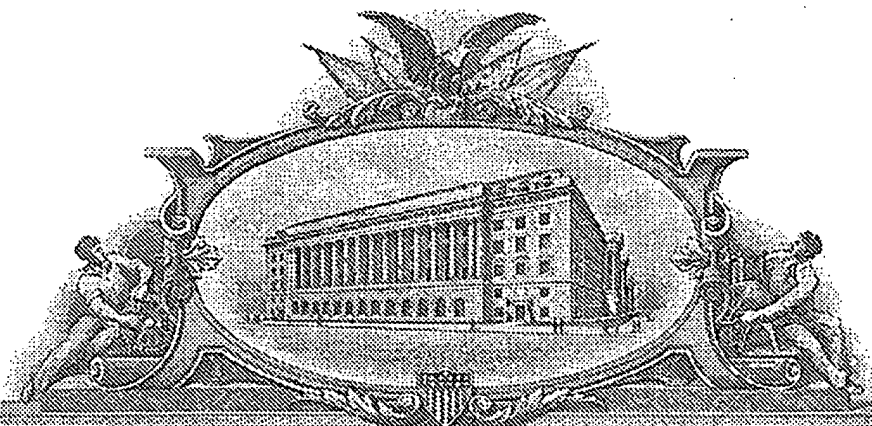
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APPLICATION NUMBER: 60/507,035

FILING DATE: *September 29, 2003*

RELATED PCT APPLICATION NUMBER: *PCT/US04/20704*



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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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2212 U.S. PTO
60/507035



INVENTOR(S)				
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BISWAJIT MARK GERRIT	CHOUDHURY ROELOFS		KINGSTON, ONTARIO, CANADA HOCKESSIN, DELAWARE	
Additional inventors are being named on the <u>p. 2</u> separately numbered sheets attached hereto				
TITLE OF THE INVENTION (500 characters max)				
TRIFLUOROSTYRENE CONTAINING COMPOUNDS GRAFTED TO BASE POLYMERS, AND THEIR USE AS POLYMER ELECTROLYTE MEMBRANES				
Direct all correspondence to: CORRESPONDENCE ADDRESS				
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ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification Number of Pages <u>39</u>				
<input type="checkbox"/> CD(s), Number				
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets <u>2</u>				
<input type="checkbox"/> Other (specify) <u></u>				
<input type="checkbox"/> Application Date Sheet. See 37 CFR 1.76				
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT				
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees.				
<input checked="" type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: <u>04-1928</u>				
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.				
				FILING FEE Amount (\$) \$160.00
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
<input checked="" type="checkbox"/> No.				
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: <u></u>				

[Page 1 of 2]

Respectfully submitted,

SIGNATURE

Daphne P. Fickes

TYPED or PRINTED NAME DAPHNE P FICKES

TELEPHONE (302) 999-6420

Date September 29, 2003

REGISTRATION NO. 36,509

(if appropriate)

Docket Number: FC0016 US PRV

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

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17668

09/29/03

U.S. PTO

PTO/SB/17 (08-03)

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**FEE TRANSMITTAL
for FY 2003**

Effective 01/01/2003. Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27**TOTAL AMOUNT OF PAYMENT (\$)** 160.00**Complete if Known**

Application Number	To Be Assigned
Filing Date	
First Named Inventor	Biswajit Choudhury Et. Al.
Examiner Name	
Art Unit	
Attorney Docket No.	FC0016 US PRV

METHOD OF PAYMENT (check all that apply)☐ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None☒ Deposit Account:

Deposit Account Number	04-1928
Deposit Account Name	E. I. du Pont de Nemours and Company

The Director is authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☒ Credit any overpayments☒ Charge any additional fee(s) during the pendency of this application☐ Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.**FEE CALCULATION****1. BASIC FILING FEE**

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
1001 750	2001 375	Utility filing fee	
1002 330	2002 165	Design filing fee	
1003 520	2003 260	Plant filing fee	
1004 750	2004 375	Reissue filing fee	
1005 160	2005 80	Provisional filing fee	160.00

SUBTOTAL (1) (\$) 160.00**2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE**

Total Claims	Extra Claims	Fee from below	Fee Paid
Independent Claims	-20** =	X 18 =	
Multiple Dependent Claims	-3** =	X 84 =	
		280 =	

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description
1202 18	2202 9	Claims in excess of 20
1201 84	2201 42	Independent claims in excess of 3
1203 280	2203 140	Multiple dependent claim, if not paid
1204 84	2204 42	** Reissue independent claims over original patent
1205 18	2205 9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) (\$) 0.00

**or number previously paid, if greater; For Reissues, see above

FEE CALCULATION (continued)**3. ADDITIONAL FEES**

Large Entity Small Entity

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
1051 130	2051 65	Surcharge - late filing fee or oath	
1052 50	2052 25	Surcharge - late provisional filing fee or cover sheet	
1053 130	1053 130	Non-English specification	
1812 2,520	1812 2,520	For filing a request for <i>ex parte</i> reexamination	
1804 920*	1804 920*	Requesting publication of SIR prior to Examiner action	
1805 1,840*	1805 1,840*	Requesting publication of SIR after Examiner action	
1251 110	2251 55	Extension for reply within first month	
1252 410	2252 205	Extension for reply within second month	
1253 930	2253 465	Extension for reply within third month	
1254 1,450	2254 725	Extension for reply within fourth month	
1255 1,970	2255 985	Extension for reply within fifth month	
1401 320	2401 160	Notice of Appeal	
1402 320	2402 160	Filing a brief in support of an appeal	
1403 280	2403 140	Request for oral hearing	
1451 1,510	1451 1,510	Petition to institute a public use proceeding	
1452 110	2452 55	Petition to revive - unavoidable	
1453 1,300	2453 650	Petition to revive - unintentional	
1501 1,300	2501 650	Utility issue fee (or reissue)	
1502 470	2502 235	Design issue fee	
1503 630	2503 315	Plant issue fee	
1460 130	1460 130	Petitions to the Commissioner	
1807 50	1807 50	Processing fee under 37 CFR 1.17(q)	
1806 180	1806 180	Submission of Information Disclosure Stmt	
8021 40	8021 40	Recording each patent assignment per property (times number of properties)	
1809 750	2809 375	Filing a submission after final rejection (37 CFR 1.129(a))	
1810 750	2810 375	For each additional invention to be examined (37 CFR 1.129(b))	
1801 750	2801 375	Request for Continued Examination (RCE)	
1802 900	1802 900	Request for expedited examination of a design application	

Other fee (specify)

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$) 0.00**SUBMITTED BY**

Name (Print/Type)	Daphne P Fickes	Registration No. (Attorney/Agent)	36,509	Telephone	(302) 999-6420
Signature	<i>Daphne P. Fickes</i>	Date	9/29/2003		

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PROVISIONAL APPLICATION COVER SHEET
Additional Page

PTO/SB/16 (08-03)

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Docket Number FC0016 US PRV

INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle [if any])	Family or Surname	Residence (City and either State or Foreign Country)
ZHEN-YU	YANG	WILMINGTON, DELAWARE

[Page 2 of 2]

Number 2 of 2

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TITLE

TRIFLUOROSTYRENE CONTAINING COMPOUNDS GRAFTED TO
BASE POLYMERS, AND THEIR USE AS POLYMER ELECTROLYTE
MEMBRANES

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FIELD OF THE INVENTION

The present invention relates to a novel compound grafted to a base polymer, and its use in electrochemical cells as membranes, and more particularly to the use of these grafted polymers in fuel cells. This invention was made with government support under Contract No. DE-FC04-02AL67606 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

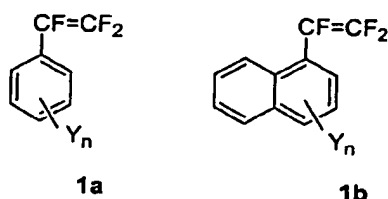
Electrochemical cells, such as fuel cells and lithium-ion batteries are known. Depending on the operating conditions, each type of cell places a particular set of requirements upon the electrolytes used in them. For fuel cells, this is typically dictated by the type of fuel, such as hydrogen or methanol, used to power the cell and the composition of the membrane used to separate the electrodes. Proton-exchange membrane fuel cells, powered by hydrogen as the fuel, could be run at higher operating temperatures than currently employed to take advantage of lower purity feed streams, improved electrode kinetics, better heat transfer from the fuel cell stack to improve its cooling. Waste heat is also employed in a useful fashion. However, if current fuel cells are to be operated at greater than 100 °C then they must be pressurized to maintain adequate hydration of typical proton-exchange membranes to support useful levels of proton conductivity.

There is an ongoing need to discover novel grafted films that improve the performance of the latest generation of electrochemical cells, such as fuel cells and lithium-ion batteries, to develop new membrane materials that will maintain adequate proton conductivity at lower levels of hydration.

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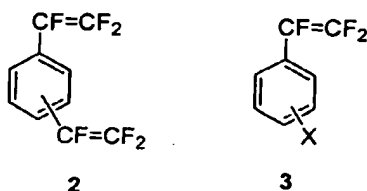
SUMMARY OF THE INVENTION

In a first aspect, the invention provides a fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure 1a, structure 1b and mixtures thereof:



wherein Y is selected from the group consisting of $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), and $-R_FSO_2N(M)SO_2R_F^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and n is between 1 and 2 for 1a, or n is between 1 and 3 for 1b.

In the first aspect, the invention also provides the grafting monomer further comprising co-monomers selected from the group consisting of compounds containing single or multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, and monomers having the structure 2, 3 or mixtures thereof:

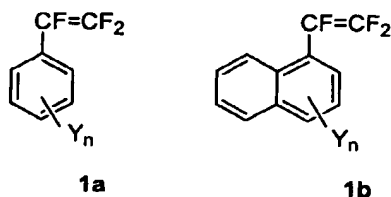


wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

In a second aspect, the invention provides a grafting process for making the ionic polymer comprising:

(a) forming a monomer composition comprising a grafting monomer, in neat form, emulsion form, or solution form; wherein the grafting monomer is selected from the group consisting of structure **1a**, structure **1b** and mixtures thereof:

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wherein Y is selected from the group consisting of $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), and $-R_FSO_2N(M)SO_2R_F^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and

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n is between 1 and 2 for **1a**, or n is between 1 and 3 for **1b**;

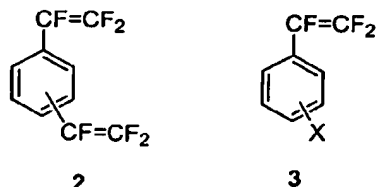
(b) irradiating a base polymer with ionizing radiation; and

15

(c) contacting the base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 to about 500 hrs. The steps (b) and (c) may be performed simultaneously or sequentially.

In the second aspect, the invention also provides the grafting monomers further comprising co-monomers selected from the group consisting of compounds containing single or multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, and monomers having the structure **2**, **3** or mixtures thereof:

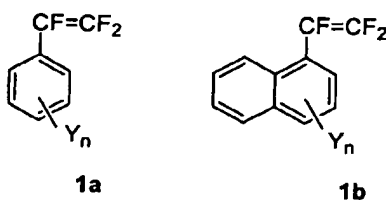
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wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

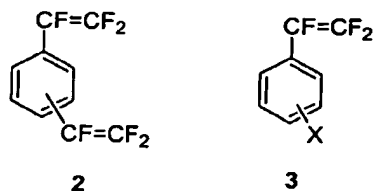
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In a third aspect, the invention provides a catalyst coated membrane comprising a polymer electrolyte membrane, wherein the polymer electrolyte membrane comprises a fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure **1a**, structure **1b** and mixtures thereof:



- wherein Y is selected from the group consisting of $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), and $-R_FSO_2N(M)SO_2R^2_F$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R^2_F groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and n is between 1 and 2 for **1a**, or n is between 1 and 3 for **1b**.

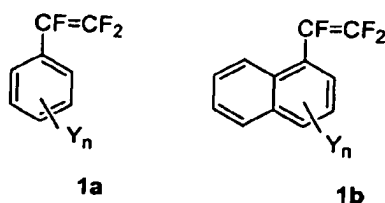
Optionally, the grafting monomers further comprise co-monomers selected from compounds containing single or multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, and monomers having the structure **2**, **3** or mixtures thereof:



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

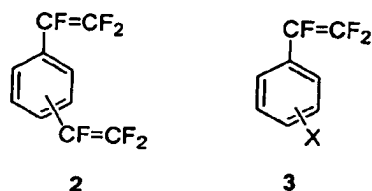
In a fourth aspect, the invention provides a membrane electrode assembly comprising a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises a fluorinated ion exchange polymer prepared by grafting a

monomer on to a base polymer film, wherein the grafting monomer is selected from the group consisting of structure **1a**, structure **1b** and mixtures thereof,



wherein Y is selected from the group consisting of $-\text{R}_\text{F}\text{SO}_2\text{F}$ (sulfonyl fluoride), $-\text{R}_\text{F}\text{SO}_3\text{M}$ (fluorosulfonic acid or salt), $-\text{R}_\text{F}\text{SO}_2\text{NH}_2$ (fluorosulfonamide), and $-\text{R}_\text{F}\text{SO}_2\text{N}(\text{M})\text{SO}_2\text{R}_\text{F}^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and n is between 1 and 2 for **1a**, or n is between 1 and 3 for **1b**.

Optionally, the grafting monomers further comprise co-monomers selected from compounds containing single or multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, and monomers having the structure **2**, **3** or mixtures thereof:

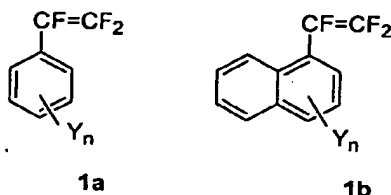


wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

In the fourth aspect, the membrane electrode assembly further comprises at least one electrode prepared from an electrocatalyst coating composition present on the first and second surfaces of the membrane. It also further comprises at least one gas diffusion backing. Alternately, the membrane electrode assembly further comprises a gas diffusion electrode present on the first and second surfaces of the membrane, wherein the

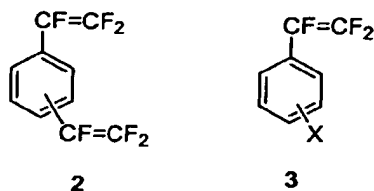
gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition.

In a fifth aspect, the invention provides an electrochemical cell, such as a fuel cell, comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises a fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure 1a, structure 1b and mixtures thereof,



wherein Y is selected from the group consisting of $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), and $-R_FSO_2N(M)SO_2R_F^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and n is between 1 and 2 for 1a, or n is between 1 and 3 for 1b.

Optionally, the grafting monomers further comprise co-monomers selected from compounds containing single or multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, and monomers having the structure 2, 3, or mixtures thereof:



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

In the fifth aspect, the fuel cell further comprises at least one electrode prepared from an electrocatalyst containing composition, e.g., an anode and a cathode, present on the first and second surfaces of the polymer electrolyte membrane. It also further comprises at least one gas diffusion backing. Alternately, the membrane electrode assembly in the fuel cell further comprises a gas diffusion electrode present on the first and second surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition.

In the fifth aspect, the fuel cell further comprises a means for delivering a fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, hydrogen or methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode. The fuel is in the liquid or vapor phase. Some suitable fuels include hydrogen; alcohols such as methanol and ethanol; ethers such as diethyl ether, etc.

BRIEF DESCRIPTION OF DRAWINGS

- Figure 1 is a schematic illustration of a single cell assembly.
- Figure 2 is a schematic illustration of the lower fixture of a four-electrode cell for in-plane conductivity measurement.

DETAILED DESCRIPTION OF THE INVENTION

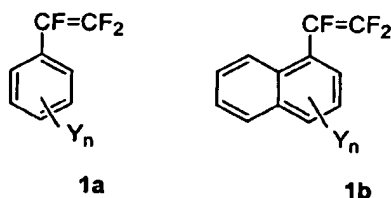
25 Fluorinated Ion Exchange Polymer:

The fluorinated ion exchange polymers of the invention are useful as polymer electrolyte membranes in fuel cells, chloralkali cells, batteries, electrolysis cells, ion exchange membranes, sensors, electrochemical capacitors, and modified electrodes.

30 Fluorinated Sulfur-Containing Monomers:

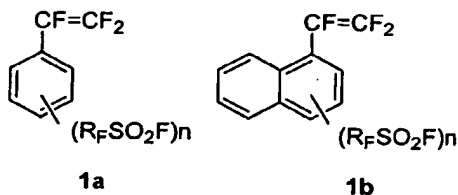
The fluorinated ion exchange polymer is made by grafting a monomer on to a base polymer, wherein the grafting monomer is selected

from the group consisting of structure **1a**, structure **1b** and mixtures thereof,



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 wherein Y is $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), or $-R_FSO_2N(M)SO_2R_F^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated alkylene, and may optionally include
 10 ether oxygens; and n is between 1 and 2 for **1a**, or n is between 1 and 3 for **1b**. Some suitable perfluorinated alkylene groups R_F , that may optionally include ether oxygens are selected from the group consisting of $(CF_2)_q$ wherein $q = 1$ to 20, $(CF_2)_qOCF_2CF_2$ wherein $q = 0$ to 12, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ wherein $q = 1$ to 8. Typically R_F is selected from
 15 the group consisting of $(CF_2)_q$ wherein $q = 1$ to 4; $(CF_2)_qOCF_2CF_2$ wherein $q = 0$ to 6; and $(CF_2CF(CF_3)O)_qCF_2CF_2$ wherein $q = 1$ to 2. R_F^2 groups typically are selected from methyl, ethyl, propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated. More typically R_F^2 groups are selected from the group consisting of perfluoromethyl,
 20 perfluoroethyl, and perfluorophenyl.

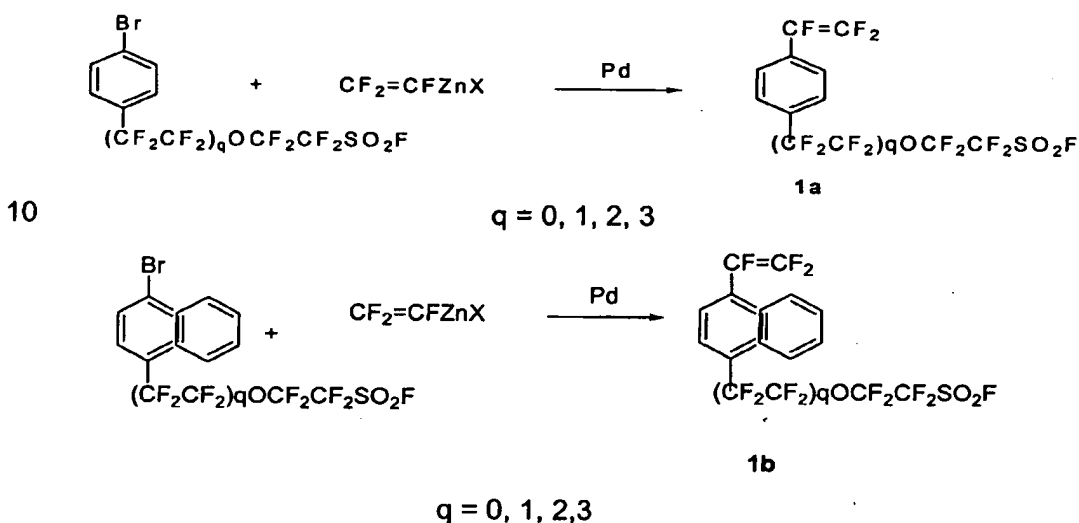
Typically the monomers having sulfonyl fluoride groups are represented by the structures **1a** or **1b**:



25 The sulfonyl fluoride groups may be converted to acid, metal salt, amide, or imide form, either before the grafting reaction or subsequent to the grafting reaction.

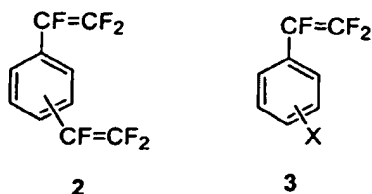
Synthesis of monomers:

- Monomer having structure **1** was prepared by Pd catalyzed reaction of trifluorovinyl zinc reagent with aryl bromide, which was obtained from A. Feiring (Feiring, et al, J. Fluorine Chem. 105, 129, 2000). The vinyl zinc reagent was made from reaction of $\text{CF}_2=\text{CFBr}$ and zinc powder in DMF (Burton et al, JOC 53, 2714, 1988).



Co-Monomers:

- 15 The grafting monomers may optionally include co-monomers to improve the grafting process, or to improve properties such as strength or resistance to solvent swelling. Co-monomers may be introduced along with monomers having structures **1a** or **1b** during the grafting reaction. The co-monomers must be capable of co-polymerization with monomers
- 20 **1a** or **1b** under free-radical conditions. Suitable crosslinking monomers comprise co-monomers selected from compounds containing multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, or compounds having structure **2**. Additional suitable co-monomers include substituted trifluorostyrene monomers having structure **3**



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen. Some suitable substituents X are hydrogen, halogen such as Cl, Br, F or I; linear or branched perfluoroalkyl groups, wherein the alkyl group
 5 comprises C1 to C10 carbon atoms; or a perfluoroalkyl group containing oxygen, chlorine or bromine, and wherein the perfluoroalkyl group comprises C1 to C10 carbon atoms. More typically, substituents X are selected from the group consisting of hydrogen, chlorine, fluorine, methyl, ethyl, methoxy, perfluoromethyl, perfluoroethyl, perfluorobutyl,
 10 perfluoromethoxy, and $-\text{CF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_3$.

Base Polymer:

The base polymer to be used as the substrate for the grafting reaction may be a homopolymer or comprised of several comonomers. The base
 15 polymer is typically selected so that it imparts desirable mechanical properties to the final grafted polymer, is stable to the irradiation used to activate the polymer for grafting, and is stable under the conditions to which it is exposed during use. For separators or membranes it is desirable that the base polymer be present in the form of a film, though
 20 other shapes may be desired depending on the electrochemical use. Suitable materials generally include homopolymers or copolymers of non-fluorinated, fluorinated, and perfluorinated monomers. Partially or completely fluorinated polymers often impart increased chemical stability and are preferred. Some typical base polymers include poly(ethylene-
 25 tetrafluoroethylene-termonomer (ETFE) that comprises a terpolymer of ethylene and tetrafluoroethylene (TFE), in the range of 35:65 to 65:35 (mole ratios) with from 1 to 10 mole% of a termonomer, perfluorobutyl ethylene in the case of DuPont Tefzel®; ETFE copolymers also using other termonomers (Neoflon® ETFE); ECTFE that comprises a copolymer

- of ethylene and chlorotrifluoroethylene; FEP that comprises a copolymer of TFE and hexafluoropropylene (HFP), optionally containing a minor amount (1-3 mol%) of perfluoro(alkyl vinyl ether) (PAVE), usually perfluoro(propyl vinyl ether) (PPVE) or perfluoro(ethyl vinyl ether) (PEVE);
- 5 PFA that comprises a copolymer of TFE and PAVE, wherein PAVE may be PPVE or PEVE; MFA that comprises a copolymer of TFE, PMVE, and PPVE; PTFE that comprises a homopolymer of TFE; modified PTFE, that contains up to 0.5 mol% of another monomer, usually a PAVE; PVF that comprises a polymer of vinyl fluoride (VF); PVDF that comprises a
- 10 polymer of vinylidene fluoride (VF₂); copolymers of VF₂ and HFP which are sold under the trademarks KynarFlex® and Viton® A by Atofina and by DuPont, respectively; polyethylene and polypropylene. The term "modified" distinguishes these polymers from copolymers of TFE. The modified PTFE polymers are, like PTFE, not melt processible.
- 15 Typically, the base polymer is selected from poly(ethylene-tetrafluoroethylene), poly(ethylene-tetrafluoroethylene-termonomer) (Tefzel®, Neoflon® ETFE); poly(tetrafluoroethylene-hexafluoropropylene) (Teflon® FEP); poly(tetrafluoroethylene-perfluorovinylether) (Teflon® PFA), polytetrafluoroethylene (Teflon® PTFE); poly(ethylene-
- 20 chlorotrifluoroethylene); poly(vinylidene fluoride) (Kynar® or Solef®); poly(vinylidene fluoride-hexafluoropropylene) (Kynar® Flex). More typically, the base polymer is selected from poly(ethylene-tetrafluoroethylene-termonomer), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoropropylvinylether),
- 25 and poly(vinylidene fluoride).

Processes for making grafted polymers and membranes:

- The fluorinated ion exchange polymer may be prepared by a grafting process comprising the steps of:
- 30 (a) forming a monomer composition comprising monomers having structures **1a** or **1b**, along with optional co-monomers, in neat form, emulsion form, or solution form

(b) irradiating a base polymer, typically in film form, with ionizing radiation

(c) contacting the base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 to about 500 hrs. The steps (b) and (c) may be performed simultaneously or sequentially.

The monomers used in the grafting process are selected from monomers of **1a** or **1b**, along with optional co-monomers, as described above under Fluorinated Ion Exchange Polymer. Base polymers suitable for the process of the second aspect generally include homopolymers or copolymers of fluorinated or perfluorinated monomers. Partially or completely fluorinated polymers often impart increased chemical stability and are preferred. Preferably the base polymer is selected from those listed earlier.

Free radicals may be created in the base polymer in order to produce attachment sites for the grafting monomers using radiation. When the base polymer is in film form, the films are known as irradiated films. The radiation dosage should be sufficient to allow for the desired graft level to be reached, but not so high as to cause excessive radiation damage. Graft level is defined as (wt. of grafted polymer – wt. of base polymer)/(wt. of base polymer). The radiation may be provided in the form of electron beam, gamma-ray, or X-rays. Electron beam irradiation is typically performed at a high dose rate that may be advantageous for commercial production. The irradiation may be done while the base polymer is in contact with the grafting monomers (simultaneous irradiation and grafting). However, if the free radicals of the base polymer are sufficiently stable, then the irradiation may be performed first and in a subsequent step the base polymer is brought into contact with the grafting monomers (post-irradiation grafting). Base polymers suitable for the post-irradiation grafting method are usually fluorinated polymers. In this case the irradiation may typically be done at sub-ambient temperatures, for example with base polymer cooled with dry ice, and it may be stored at a

sufficiently low temperature to prevent decay of the free radicals prior to its use in the grafting reaction.

With some substrates, such as poly(ethylene-tetrafluoroethylene) the irradiation may be performed in the presence of oxygen or in an oxygen-free environment, and an appreciable graft level can be obtained in either case. It is preferred to perform the grafting in an inert-gas, such as nitrogen or argon. This may be accomplished by loading the base polymer films, within an inert-atmosphere box, into oxygen-barrier bags, sealing them shut (with or without grafting monomers and solvent), and then irradiating. In the case of post-irradiation grafting, the base polymer may then also be stored in the oxygen-free environment before and during the grafting reaction.

The grafting reaction is performed by exposing the base polymer to a monomer composition containing the grafting monomers. In simplest form the neat liquid monomers may be used as the monomer composition. It is generally desirable to lower the quantity of fluorinated monomer used in the grafting reaction, and this may be accomplished by diluting it by forming an emulsion or a solution with a solvent, which thus increases the total working volume of the grafting composition. The monomer composition may thus be an emulsion made by mechanical or ultrasonic mixing of the monomers with water and/or alcohols such as isopropanol, and fluorinated or non-fluorinated surfactants such as fluorinated carboxylic salts, typically ammonium perfluorooctanoate and ammonium fluorooctanesulfonate. A third useful form for the monomer composition is a solution of the monomers in an inert organic solvent. Typical solvents include toluene, benzene, halobenzenes, fluorocarbons such as perfluoroethers, fluorochlorocarbons such as 1,1,2-trichlorotrifluoroethane, chlorocarbons such as CH_2Cl_2 , $\text{CH}_2\text{ClCH}_2\text{Cl}$, and hydrocarbons. The process for making grafted polymers by solvent grafting may also use fluoroalkyl benzene solvents. Preferred fluoroalkyl benzene solvents are trifluoromethylbenzene (α,α,α -trifluorotoluene), 1,3-bis(trifluoromethyl)benzene, and 1,4-bis(trifluoromethyl)benzene, and (pentafluoroethyl)benzene, with trifluoromethylbenzene being most

preferred. We have found that aromatic compounds substituted with fluorinated aliphatic groups, when used as solvents for the fluorinated vinyl monomers, provide fast rates for grafting monomers to fluorinated base polymers. The grafting solution may comprise mixtures of the grafting monomer(s) and the solvent, where the mole fraction of the solvent in the mixture is between 1% and 99%, more typically between 5% and 90%. Grafting is accomplished by contacting the base polymer films, during irradiation or subsequent to irradiation, with the monomer composition and holding films at 0 °C to 120 °C for 0.1 to 500 hrs. Typical temperatures are 25 °C to 100 °C, more typically 35 to 90 °C, and most typically 40 to 80 °C. Typical times are 10 min to 300 hrs, more typically 1 hr to 200 hrs, and most typically 1 hour to 100 hours. Subsequent to the grafting reaction, the solvent and unreacted monomer may be removed by extraction with a low-boiling solvent or through vaporization. The grafted polymer may also be extracted with a solvent in order to remove any polymer formed in the film that is not grafted to the base film.

Preparation of Ionic Polymers:

One of the advantages of the current invention over prior art of grafted membranes is the facile conversion of the fluorosulfonyl fluorides to acid form, without the use of sulfonation reagents. Polymers grafted with the monomers bearing pendant sulfonyl fluoride groups can be hydrolyzed with bases such as MOH or M_2CO_3 ($M = Li, Na, K, Cs, NH_4$) or MOH in MeOH and/or DMSO, and water. The hydrolysis is usually carried out at room temperature to 100°C, preferably at room temperature to 80°C. Treatment of polymeric salts with acids such as HNO_3 gave polymeric acids. With polymeric substrates such as PVDF that are sensitive to strong base, it is preferable to use the weaker carbonate bases that avoid decomposition of the substrate.

Electrochemical Cell:

As shown in Figure 1, an electrochemical cell, such as a fuel cell, comprises a catalyst coated membrane (CCM) (10) in combination with at

least one gas diffusion backing (GDB) (13) to form an unconsolidated membrane electrode assembly (MEA). The catalyst coated membrane (10) comprises a polymer electrolyte membrane (11) discussed above and catalyst layers or electrodes (12) formed from an electrocatalyst coating composition. The fuel cell is further provided with an inlet (14) for fuel, such as hydrogen; liquid or gaseous alcohols, e.g. methanol and ethanol; or ethers, e.g. diethyl ether, etc., an anode outlet (15), a cathode gas inlet (16), a cathode gas outlet (17), aluminum end blocks (18) tied together with tie rods (not shown), a gasket for sealing (19), an electrically insulating layer (20), graphite current collector blocks with flow fields for gas distribution (21), and gold plated current collectors (22).

Alternately, gas diffusion electrodes comprising a gas diffusion backing having a layer of an electrocatalyst coating composition thereon may be brought into contact with a solid polymer electrolyte membrane to form the MEA.

The electrocatalyst coating compositions used to apply the catalyst layers as electrodes on the CCM (10) or the GDE comprise a combination of catalysts and binders dispersed in suitable solvents for the binders, and may include other materials to improve electrical conductivity, adhesion, and durability. The catalysts may be unsupported or supported, typically on carbon, and may differ in composition depending on their use as anodes or cathodes. The binders typically consist of the same polymer used to form the polymer electrolyte membrane (11), but may contain in part or be solely composed of other suitable polymer electrolytes as needed to improve the operation of the fuel cell. Some examples include Nafion® perfluorosulfonic acid, sulfonated polyether sulfones, or their membranes.

The fuel cell utilizes a fuel source that may be in the gas or liquid phase, and may comprise hydrogen, an alcohol, or an ether. The fuel is humidified to the degree required to maintain adequate ionic conductivity in the solid polymer electrolyte membrane discussed above so that the fuel cell provides a high power output. Depending on the operating temperature, the fuel cell may be operated at elevated pressures to maintain the required degree of humidification. Typically a gaseous humidified hydrogen feed or methanol/water solution is supplied to the

anode compartment, and air or oxygen supplied to the cathode compartment.

Catalyst Coated Membrane:

5 A variety of techniques are known for CCM manufacture, which apply an electrocatalyst coating composition similar to that described above onto a solid polymer electrolyte membrane. Some known methods include spraying, painting, patch coating and screen, decal, pad or flexographic printing.

10 In one embodiment of the invention, the MEA (30), shown in Figure 1, may be prepared by thermally consolidating the gas diffusion backing (GDB) with a CCM at a temperature of under 200 °C, preferably 140-160 °C. The CCM may be made of any type known in the art. In this embodiment, an MEA comprises a solid polymer electrolyte (SPE)
15 membrane with a thin catalyst-binder layer disposed thereon. The catalyst may be supported (typically on carbon) or unsupported. In one method of preparation, a catalyst film is prepared as a decal by spreading the electrocatalyst coating composition on a flat release substrate such as Kapton® polyimide film (available from the DuPont Company). After the
20 coating dries, the decal is transferred to the surface of the SPE membrane by the application of pressure and heat, followed by removal of the release substrate to form a catalyst coated membrane (CCM) with a catalyst layer having a controlled thickness and catalyst distribution. Alternatively, the catalyst layer is applied directly to the membrane, such as by printing, and
25 the catalyst film is then dried at a temperature not greater than 200 °C.

 The CCM, thus formed, is then combined with a GDB to form the MEA (30). The MEA is formed, by layering the CCM and the GDB, followed by consolidating the entire structure in a single step by heating to a temperature no greater than 200 °C, preferably in the range of 140-160
30 °C, and applying pressure. Both sides of the MEA can be formed in the same manner and simultaneously. Also, the composition of the catalyst layer and GDB could be different on opposite sides of the membrane.

 The invention is illustrated in the following examples.

EXAMPLES

In-Plane Conductivity Measurement

The in-plane conductivity of membranes was measured under

5 conditions of controlled relative humidity and temperature by a technique in which the current flowed parallel to the plane of the membrane. A four-electrode technique was used similar to that described in an article entitled

10 "Proton Conductivity of Nafion® 117 As Measured by a Four-Electrode AC Impedance Method" by Y. Sone et al., J. Electrochem. Soc., 143,1254 (1996), which is herein incorporated by reference. Referring to Figure 2, a

lower fixture (40) was machined from annealed glass-fiber reinforced PEEK to have four parallel ridges (41) containing grooves that supported and held four 0.25 mm diameter platinum wire electrodes. The distance

15 between the two outer electrodes was 25 mm, while the distance between the two inner electrodes was 10 mm. A strip of membrane was cut to a width between 10 and 15 mm and a length sufficient to cover and extend slightly beyond the outer electrodes, and placed on top of the platinum electrodes. An upper fixture (not shown), which had ridges corresponding

20 in position to those of the bottom fixture, was placed on top and the two fixtures were clamped together so as to push the membrane into contact with the platinum electrodes. The fixture containing the membrane was placed inside a small pressure vessel (pressure filter housing), which was placed inside a forced-convection thermostated oven for heating. The temperature within the vessel was measured by means of a thermocouple.

25 Water was fed from a calibrated Waters 515 HPLC pump (Waters Corporation, Milford, MA) and combined with dry air fed from a calibrated mass flow controller (200 sccm maximum) to evaporate the water within a coil of 1.6 mm diameter stainless steel tubing inside the oven. The resulting humidified air was fed into the inlet of the pressure vessel. The

30 total pressure within the vessel (100 to 345 kPa) was adjusted by means of a pressure-control let-down valve on the outlet and measured using a capacitance manometer (Model 280E, Setra Systems, Inc., Boxborough, MA). The relative humidity was calculated assuming ideal gas behavior

using tables of the vapor pressure of liquid water as a function of temperature, the gas composition from the two flow rates, the vessel temperature, and the total pressure. Referring to Figure 2, the slots (42) in the lower and upper parts of the fixture allowed access of humidified air to the membrane for rapid equilibration with water vapor. Current was applied between the outer two electrodes while the resultant voltage was measured between the inner two electrodes. The real part of the AC impedance (resistance) between the inner two electrodes, R , was measured at a frequency of 1 kHz using a potentiostat/frequency response analyzer (PC4/750™ with EIS software, Gamry Instruments, Warminster, PA). The conductivity, κ , of the membrane was then calculated as

$$\kappa = 1.00 \text{ cm} / (R \times t \times w),$$

where t was the thickness of the membrane and w was its width (both in cm).

Example 1: Irradiated Films

ETFE films were obtained in thicknesses of 27 μm and 65 μm (Tefzel® LZ5100 and LZ5200, DuPont Company, Wilmington, DE). PVdF films were obtained with a thickness 50 μm (Kynar® Goodfellow Corp, Berwyn, PA). The films were degassed and brought into a nitrogen-filled glove box. They were cut to size and sealed inside gas-barrier bags (ESCAL® ceramic-barrier bag from Mitsubishi Gas Chemical America, Inc. or PPD aluminum-foil-barrier bags from Shield Pack, Inc., West Monroe, LA). Dry ice pellets were placed in a metal tray for cooling and the bags with films were placed into the metal tray. The films were irradiated using an electron beam accelerator using 1 MV and a current of 2 mA. Up to 6 films were placed in each bag, and the bags were stacked up to 2 high in the tray. The beam was electronically scanned across a 40" aperture while the metal tray was moved slowly beneath the beam. Each pass resulted in a dosage of 20 kGy, and from 1 to 15 passes were used

resulting in total dosages between 20 and 300 kGy. The irradiated films were stored in the bags under dry ice or in a refrigerator cooled to -40°C .

Example 2: Solvent Grafting

- 5 Irradiated films from Example 1 with 140 kGy dosage were weighed and placed inside a glass jar inside a dry box filled with nitrogen. A solution of $\text{CF}_2=\text{CF}-\text{C}_6\text{H}_4\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$ and α,α,α -trifluorotoluene (1:1 v:v) was poured over the films and a Teflon® mesh was used to hold the films under the solution. The jar was covered and heated to 60°C for 25 hr. The films
- 10 were removed from the monomer solution and rinsed briefly with α,α,α -trifluorotoluene. The grafted films were dried in a vacuum oven at 22°C with nitrogen bleed for 16 hours. The films were then heated in tetrahydrofuran (THF) at 70°C for 4 hours to further remove residual solvent, monomer, and/or polymer which was not bonded to the base film.
- 15 The films were dried under ambient conditions in a fume hood, reweighed, and the uptake calculated. Uptake was calculated as $(w_g - w)/w$, where w is the initial weight of the film and w_g is the weight of the dried grafted film after the THF extraction.

Film	Initial thickness (um)	Thickness after grafting (um)	Wt uptake (%)
PVdF	62	72	145
ETFE	27	39	257
ETFE	65	82	284

20

Example 3: Hydrolysis and Conductivity

A $65\text{ }\mu\text{m}$ ETFE film with 140 kGy dose was grafted similar to the procedure of Example 2, except the grafting time was increased to 100 hr. The grafted film had a thickness of $79\text{ }\mu\text{m}$ and a weight uptake of 236%.

- 25 The film was hydrolyzed in 10 wt% KOH in H_2O : MeOH: DMSO 5:4:1

wt:wt:wt in a Petri dish @ 50 °C overnight (16 hours). The film was rinsed in deionized water for 5 minutes at ambient temperature. The film was ion-exchanged to acid form by dipping in 14% nitric acid at 50 °C for 1 hr, followed by rinsing in deionized water and then three successive soaks in deionized water for 15 minutes each at 50 °C with changing to fresh water after each soak. The hydrolyzed sample was swollen to 107 µm thickness. The conductivity of the membrane was measured in-plane, as described above, immersed in water, at ambient temperature, and was found to be 159 mS/cm. The conductivity of the sample was measured in-plane at 120 °C under controlled humidity varying from 25% first to 95% at the end, after which the sample thickness had shrunk to 84 µm with also a shrinkage in the width. The conductivity values are given in the table below:

RH %	Conductivity (mS/cm)
25	31
50	111
95	511

Example 4: Emulsion Grafting

A 0.5 L two or three necked clean flask fitted with condenser topped with a N₂ inlet/outlet, and a stirring bar was charged with 100 mL of deionized water and 8.4 mL of 20% ammonium perfluorooctanoate (C8) solution. The solution was bubbled with N₂ for 30 min. 15 g (42.4 mmol) of CF₂=CFC₆H₄OCF₂CF₂SO₂F was added. The resulting mixture was ultrasonicated for 5 min to give milky emulsion.

Irradiated films from Example 1, with 20 kGy dosage, were weighed and placed inside a glass jar inside a dry box filled with nitrogen. The emulsion made above was transferred into the glass jar under nitrogen and a Teflon® mesh was used to hold the films under the emulsion. The jar was covered under N₂ and heated with stirring at 70 °C. The films were removed from the jar after time specified in the Table below and washed with MeOH, acetone and water. The grafted films were dried in a vacuum

oven at 70 °C with nitrogen bleed overnight and then were heated in THF at 70 °C for 4 hours to further remove residual monomer and/or polymer which was not bonded to the base film. The films were dried in a vacuum oven at 70 °C with nitrogen bleed, re-weighed, and the uptake calculated.

- 5 Uptake was calculated as $(w_g - w)/w$, where w is the initial weight of the film and w_g is the weight of the dried grafted film after the THF extraction.

Film	Time (h)	Init. Weight (g)	Final Weight (g)	Wt uptake (%)
PVdF(1 mil)	24	0.106	0.215	102.8
PVdF (1 mil)	48	0.111	0.225	102.7
PVdF (1 mil)	72	0.103	0.213	106.8
ETFE (2 mil)	24	0.200	0.393	96.5
ETFE (2 mil)	48	0.225	0.454	101.8
ETFE (2 mil)	72	0.216	0.450	108.3

Example 5: Emulsion Grafting

- 10 A 0.5 L two or three necked clean flask fitted with condenser topped with a N₂ inlet/outlet, and a stirring bar was charged with 100 mL of deionized water and 8.4 mL of 20% C8 solution. The solution was bubbled with N₂ for 30 min. 15 g (42.4 mmol) of CF₂=CFC₆H₄OCF₂CF₂SO₂F were added. The resulting mixture was
- 15 ultrasonicated for 5 min to give a milky emulsion.

- Irradiated films from Example 1 with 40 kGy dosage were weighed and placed inside a glass jar inside a dry box filled with nitrogen. The emulsion made above was transferred into the glass jar under nitrogen and a Teflon® mesh was used to hold the films under the emulsion. The
- 20 jar was covered under N₂ and heated with stirring at 70 °C. The films were removed from the jar after certain time and washed with MeOH, acetone and water. The grafted films were dried in a vacuum oven at 70 °C with nitrogen bleed over night and then were heated in THF at 70 °C for 4

hours to further remove residual monomer and/or polymer that was not bonded to the base film. The films were dried in a vacuum oven at 70 °C with nitrogen bleed, re-weighed, and the uptake calculated. Uptake was calculated as $(w_g - w)/w$, where w is the initial weight of the film and w_g is the weight of the dried grafted film after the THF extraction.

Film	Time (h)	Init. Weight (g)	Final Weight (g)	Wt uptake (%)
ETFE (2 mil)	24	0.237	0.279	23.2
ETFE (2 mil)	48	0.211	0.311	50.2

Example 6: Emulsion Grafting

A 0.5 L, two or three necked, clean flask fitted with condenser topped with a N₂ inlet/outlet, and a stirring bar was charged with 100 mL of deionized water and 8.4 mL of 20% C8 solution. The solution was bubbled with N₂ for 30 min. 15 g (42.4 mmol) of CF₂=CFC₆H₄OCF₂CF₂SO₂F were added. The resulting mixture was ultrasonicated for 5 min to give a milky emulsion.

Irradiated films from Example 1 with 140 kGy dosage were weighed and placed inside a glass jar inside a dry box filled with nitrogen. The emulsion made above was transferred into the glass jar under nitrogen and a Teflon® mesh was used to hold the films under the emulsion. The jar was covered under N₂ and heated with stirring at 70 °C. The films were removed from the jar after certain time and washed with MeOH, acetone and water. The grafted films were dried in a vacuum oven at 70°C with nitrogen bleed overnight and then were heated in THF at 70 °C for 4 hours to further remove residual monomer and/or polymer which was not bonded to the base film. The films were dried in a vacuum oven at 70°C with nitrogen bleed, reweighed, and the uptake calculated. Uptake was calculated as $(w_g - w)/w$, where w is the initial weight of the film and w_g is the weight of the dried grafted film after the THF extraction.

Film	Time (h)	Init. Weight (g)	Final Weight (g)	Wt uptake (%)
ETFE(1 mil)	8	0.097	0.234	141.2
ETFE (1 mil)	24	0.116	0.477	311.2
ETFE (1 mil)	48	0.106	0.539	408.5
ETFE (1 mil)	72	0.102	0.520	409.8
ETFE (1 mil)	72	0.465	0.2.333	401.7

Example 7. Emulsion Grafting

A 0.5 L two or three necked clean flask fitted with condenser topped with a N₂ inlet/outlet, a stirring bar was charged with 100 mL of deionized water and 8.4 mL of 20% C8 solution. The solution was bubbled with N₂ for 30 min. 15 g (42.4 mmol) of CF₂=CFC₆H₄OCF₂CF₂SO₂F were added. The resulting mixture was ultrasonicated for 5 min to give milky emulsion.

Irradiated films from Example 1 with 300 kGy dosage were weighed and placed inside a glass jar inside a dry box filled with nitrogen. The emulsion made above was transferred into the glass jar under nitrogen and a Teflon® mesh was used to hold the films under the emulsion. The jar was covered under and heated with stirring at 70 °C. The films were removed from the jar after certain time and washed with MeOH, acetone and water. The grafted films were dried in a vacuum oven at 70°C with nitrogen bleed over night and were then heated in THF at 70 °C for 4 hours to further remove residual monomer and/or polymer which was not bonded to the base film. The films were dried in a vacuum oven at 70°C with nitrogen bleed, reweighed, and the uptake calculated. Uptake was calculated as $(w_g - w)/w$, where w is the initial weight of the film and w_g is the weight of the dried grafted film after the THF extraction.

Film	Time (h)	Init. Weight (g)	Final Weight (g)	Wt uptake (%)
ETFE (2 mil)	3	0.197	0.211	7.1
ETFE (2 mil)	11	0.244	0.300	22.9
ETFE (2 mil)	30	0.212	0.322	51.9
ETFE (2 mil)	55	0.199	0.555	178.8
ETFE (2 mil)	120	0.897	3.172	253.6

Example 8. Hydrolysis and Conductivity

A grafted 1 mil ETFE film having 141% weight gain was immersed in 10 wt% KOH in H₂O: MeOH: DMSO 5:4:1 wt:wt:wt in a Petri dish @ 50 °C overnight two days. The film was rinsed in deionized water for 5 minutes at ambient temperature. The film was ion-exchanged to acid form by dipping in 14% nitric acid at 50 °C for 2 hr twice, followed by rinsing in deionized water and then three successive soaks in deionized water for 15 minutes at room temperature and then boiled in water for 1 hr. The hydrolyzed sample was swollen to 36 µm thickness. The conductivity of the sample was measure in-plane at 120 °C under controlled humidity varying from 25% first to 95% at the end. The conductivity values are given in the table below:

RH %	Conductivity (mS/cm)
25	17.7
50	69.8
95	368.3

Example 9. Hydrolysis and Conductivity

A grafted 2 mil ETFE film having 23.2 % weight gain was immersed in 10 wt% KOH in H₂O: MeOH: DMSO 5:4:1 wt:wt:wt in a Petri dish @ 50 °C for two days. The film was rinsed in deionized water for 5

minutes at ambient temperature. The film was ion-exchanged to acid form by dipping in 14% nitric acid at room temperature for 2 days, followed by rinsing in deionized water and to neutral and dried in an vacuum oven at 60°C. The hydrolyzed sample was swollen to 64 μm thickness. The

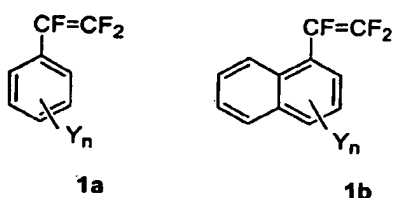
- 5 conductivity of the sample was measure in-plane at 120 °C under controlled humidity varying from 25% first to 95% at the end. The conductivity values are given in the table below:

RH %	Conductivity (mS/cm)
25	0.55
50	3.95
95	43.5

CLAIMS

What is claimed is:

1. A fluorinated ion exchange polymer prepared by grafting a
5 monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure 1a, structure 1b and mixtures thereof,



10

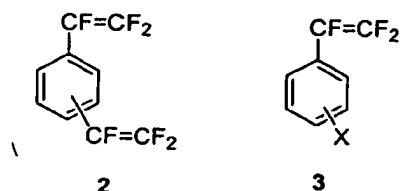
wherein Y is selected from the group consisting of $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), and $-R_FSO_2N(M)SO_2R_F^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and
15 n is between 1 and 2 for 1a, or n is between 1 and 3 for 1b.

2. The fluorinated ion exchange polymer of claim 1 wherein Y is $-R_FSO_2F$.

3. The fluorinated ion exchange polymer of claim 1 wherein R_F is
20 selected from the group consisting of $(CF_2)_q$ wherein $q = 1$ to 20, $(CF_2)_qOCF_2CF_2$ wherein $q = 0$ to 12, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ wherein $q = 1$ to 8, and R_F^2 is selected from the group consisting of methyl, ethyl, propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated.

- 25 4. The fluorinated ion exchange polymer of claim 3 wherein R_F is selected from the group consisting of $(CF_2)_q$ wherein $q = 1$ to 4, $(CF_2)_qOCF_2CF_2$ wherein $q = 0$ to 6, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ wherein $q = 1$ to 2, and R_F^2 is selected from the group consisting of perfluoromethyl, perfluoroethyl, and perfluorophenyl.

5. The fluorinated ion exchange polymer of claim 1 wherein the grafting monomers further comprise co-monomers selected from the group consisting of compounds containing a single vinyl group, compounds containing multiple vinyl groups, monomers having the structure 2, monomers having structure 3 and mixtures thereof:



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

6. The fluorinated ion exchange polymer of claim 5 wherein the compounds containing single or multiple vinyl groups are divinyl benzene or triallyl cyanurate.

7. The fluorinated ion exchange polymer of claim 5 wherein the substituents X on co-monomer of structure 3 are selected from the group consisting of hydrogen, halogen; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; and a perfluoroalkyl group containing oxygen, chlorine or bromine, wherein the perfluoroalkyl group comprises C1 to C10 carbon atoms.

8. The fluorinated ion exchange polymer of claim 7 wherein the substituents X on co-monomer of structure 3 are selected from the group consisting of hydrogen, chlorine, fluorine, methyl, ethyl, methoxy, perfluoromethyl, perfluoroethyl, perfluorobutyl, perfluoromethoxy, and $-\text{CF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_3$.

9. The fluorinated ion exchange polymer of claim 1 wherein the base polymer is a homopolymer or copolymer of non-fluorinated, fluorinated, and perfluorinated monomers.

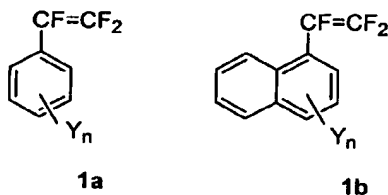
10. The fluorinated ion exchange polymer of claim 9 wherein the base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene), poly(ethylene-chlorotrifluoroethylene),

poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoroalkyl vinyl ether), poly(tetrafluoroethylene-perfluoromethyl vinyl ether), poly(tetrafluoroethylene-perfluoropropyl vinyl ether), polytetrafluoroethylene, modified polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, poly(vinylidene fluoride-hexafluoropropylene), polyethylene, and polypropylene.

11. The fluorinated ion exchange polymer of claim 10 wherein the perfluoro(alkyl vinyl ether), is perfluoro(propyl vinyl ether) or perfluoro(ethyl vinyl ether).

12. The fluorinated ion exchange polymer of claim 2 wherein the base polymer comprises a terpolymer of ethylene, tetrafluoroethylene (TFE), and 1 to 10 mole% of a termonomer such as perfluorobutyl ethylene.

13. A fluorinated ion exchange polymer membrane comprising a fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure **1a**, structure **1b** and mixtures thereof,



20

wherein Y is selected from the group consisting of $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), and $-R_FSO_2N(M)SO_2R_F^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and

25

n is between 1 and 2 for **1a**, or n is between 1 and 3 for **1b**; and wherein the base polymer is a partially or completely fluorinated polymer in film form.

14. The fluorinated ion exchange membrane of claim 13 wherein the base polymer is a completely fluorinated polymer.

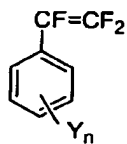
15. The fluorinated ion exchange membrane of claim 13 wherein the base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene), poly(ethylene-tetrafluoroethylene-termonomer),
5 poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluorovinylether), polytetrafluoroethylene, poly(ethylene-chlorotrifluoroethylene); poly(vinylidene fluoride), and poly(vinylidene fluoride-hexafluoropropylene).

16. The fluorinated ion exchange membrane of claim 15 wherein the base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene-termonomer), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoropropylvinylether), and poly(vinylidene fluoride).

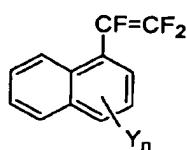
17. The fluorinated ion exchange membrane of claim 15 wherein the base polymer comprises a terpolymer of ethylene, tetrafluoroethylene (TFE), and 1 to 10 mole% of a perfluorobutyl ethylene.

18. A grafting process for making the fluorinated ion exchange polymer membrane comprising:

20 forming an monomer composition comprising a grafting monomer, in neat form, emulsion form, or solution form, wherein the grafting monomer is selected from the group consisting of structure 1a, structure 1b and mixtures thereof,



1a



1b

wherein Y is selected from the group consisting of $-\text{R}_\text{F}\text{SO}_2\text{F}$ (sulfonyl fluoride), $-\text{R}_\text{F}\text{SO}_3\text{M}$ (fluorosulfonic acid or salt), $-\text{R}_\text{F}\text{SO}_2\text{NH}_2$ (fluorosulfonamide), and $-\text{R}_\text{F}\text{SO}_2\text{N}(\text{M})\text{SO}_2\text{R}_\text{F}^2$ (imide); wherein M is H, an

alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and

n is between 1 and 2 for **1a**, or n is between 1 and 3 for **1b**;

(b) irradiating a base polymer with ionizing radiation, and

5 (c) contacting the base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 to about 500 hrs.

19. The process of claim 18 wherein the base polymer is in film form.

10 20. The process of claim 18 wherein steps (b) and (c) are performed simultaneously.

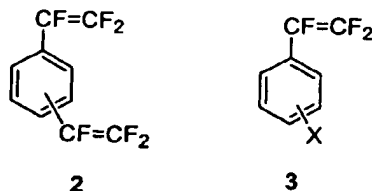
21. The process of claim 18 wherein steps (b) and (c) are performed sequentially.

22. The process of claim 18 wherein Y is $-R_FSO_2F$.

15 23. The process of claim 18 wherein R_F is selected from the group consisting of $(CF_2)_q$ wherein $q = 1$ to 20, $(CF_2)_qOCF_2CF_2$ wherein $q = 0$ to 12, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ wherein $q = 1$ to 8, and R_F^2 is selected from the group consisting of methyl, ethyl, propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated.

20 24. The process of claim 23 wherein R_F is selected from the group consisting of $(CF_2)_q$ wherein $q = 1$ to 4, $(CF_2)_qOCF_2CF_2$ wherein $q = 0$ to 6, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ wherein $q = 1$ to 2, and R_F^2 is selected from the group consisting of perfluoromethyl, perfluoroethyl, and perfluorophenyl.

25 25. The process of claim 18 wherein the grafting monomer further comprises co-monomers selected from the group consisting of compounds containing a single vinyl group, compounds containing multiple vinyl groups, monomers having the structure **2**, monomers having structure **3** and mixtures thereof:



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

26. The process of claim 25 wherein the compounds containing
5 single or multiple vinyl groups are divinyl benzene or triallyl cyanurate.

27. The process of claim 25 wherein the substituents X on co-
monomer of structure 3 are selected from the group consisting of
hydrogen, halogen; linear or branched perfluoroalkyl groups, wherein the
alkyl group comprises C1 to C10 carbon atoms; and a perfluoroalkyl group
10 containing oxygen, chlorine or bromine, wherein the perfluoroalkyl group
comprises C1 to C10 carbon atoms.

28. The process of claim 18 wherein the base polymer is a
homopolymer or copolymer of non-fluorinated, fluorinated, and
perfluorinated monomers.

15 29. The process of claim 28 wherein the base polymer is selected
from the group consisting of poly(ethylene-tetrafluoroethylene),
poly(ethylene-chlorotrifluoroethylene), poly(tetrafluoroethylene-
hexafluoropropylene), poly(tetrafluoroethylene-perfluoroalkyl vinyl ether),
poly(tetrafluoroethylene-perfluoromethyl vinyl ether),
20 poly(tetrafluoroethylene-perfluoropropyl vinyl ether),
polytetrafluoroethylene, modified polytetrafluoroethylene, polyvinyl
fluoride, polyvinylidene fluoride, poly(vinylidene
fluoride-hexafluoropropylene), polyethylene, and polypropylene.

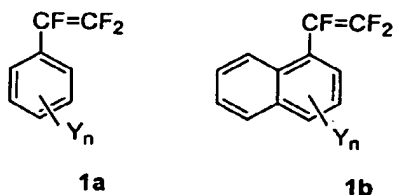
25 30. The process of claim 28 wherein the base polymer is a partially
or completely fluorinated polymer.

31. The process of claim 30 wherein the base polymer is selected
from the group consisting of poly(ethylene-tetrafluoroethylene),
poly(ethylene-tetrafluoroethylene-termonomer), poly(tetrafluoroethylene-
hexafluoropropylene), poly(tetrafluoroethylene-perfluorovinylether),

polytetrafluoroethylene, poly(ethylene-chlorotrifluoroethylene);
poly(vinylidene fluoride), and poly(vinylidene fluoride-
hexafluoropropylene).

32. A catalyst coated membrane comprising a polymer electrolyte
5 membrane having a first surface and a second surface, wherein the
polymer electrolyte membrane comprises a fluorinated ion exchange
polymer prepared by grafting a monomer on to a base polymer, wherein
the grafting monomer is selected from the group consisting of structure **1a**,
structure **1b** and mixtures thereof,

10



- wherein Y is $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or
salt), $-R_FSO_2NH_2$ (fluorosulfonamide), or $-R_FSO_2N(M)SO_2R_F^2$ (imide);
15 wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are
perfluorinated or partially fluorinated, and may optionally include ether
oxygens; and

n is between 1 and 2 for **1a**, or n is between 1 and 3 for **1b**.

33. The catalyst coated membrane of claim 32 wherein the base
20 polymer is in film form.

34. The catalyst coated membrane of claim 32 further comprising at
least one electrode prepared from an electrocatalyst coating composition
present on the first and second surfaces of the polymer electrolyte
membrane.

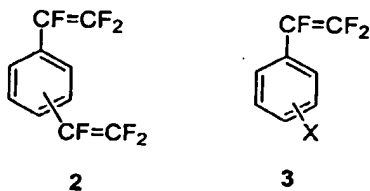
- 25 35. The catalyst coated membrane of claim 34 wherein the at least
one electrode is an anode.

36. The catalyst coated membrane of claim 34 wherein the at least
one electrode is a cathode.

37. The catalyst coated membrane of claim 34 wherein the electrocatalyst coating composition comprises a catalyst and a binder.

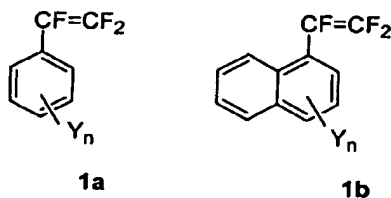
38. The catalyst coated membrane of claim 37 wherein the binder is a perfluorosulfonic acid polymer.

5 39. The catalyst coated membrane of claim 32 wherein the grafting monomer further comprises co-monomers selected from the group consisting of compounds containing a single vinyl group, compounds containing multiple vinyl groups, monomers having the structure 2, monomers having structure 3 and mixtures thereof:



10 wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

40. A membrane electrode assembly comprising a polymer electrolyte membrane, having a first surface and a second surface,
15 wherein the polymer electrolyte membrane comprises a fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure 1a, structure 1b and mixtures thereof,



20 wherein Y is $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), or $-R_FSO_2N(M)SO_2R_F^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2
25 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and

n is between 1 and 2 for **1a**, or n is between 1 and 3 for **1b**.

41. The membrane electrode assembly of claim 40 wherein the base polymer is in film form.

42. The membrane electrode assembly of claim 40 further
5 comprising at least one electrode prepared from an electrocatalyst coating composition present on the first or second surfaces of the membrane.

43. The membrane electrode assembly of claim 42 wherein at least one electrode is an anode.

44. The membrane electrode assembly of claim 42 wherein at least
10 one electrode is a cathode.

45. The membrane electrode assembly of claim 42 wherein the electrocatalyst coating composition comprises a catalyst and a binder.

46. The membrane electrode assembly of claim 45 wherein the binder is a perfluorosulfonic acid polymer.

47. The membrane electrode assembly of claim 40 further
15 comprising at least one gas diffusion backing adjacent at least one electrode present on the polymer electrolyte membrane.

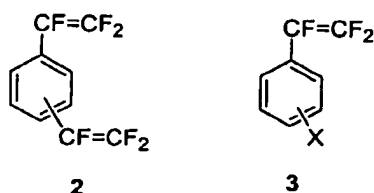
48. The membrane electrode assembly of claim 40 further
comprising at least one gas diffusion electrode present on the first or
20 second surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst coating composition.

49. The membrane electrode assembly of claim 40 wherein Y is $-R_FSO_2F$.

25 50. The membrane electrode assembly of claim 40 wherein R_F is selected from the group consisting of $(CF_2)_q$ wherein $q = 1$ to 20, $(CF_2)_qOCF_2CF_2$ wherein $q = 0$ to 12, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ wherein $q = 1$ to 8, and R_F^2 is selected from the group consisting of methyl, ethyl,

propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated.

51. The membrane electrode assembly of claim 40 wherein the grafting monomers further comprise co-monomers selected from the group consisting of compounds containing a single vinyl group, compounds containing multiple vinyl groups, monomers having the structure 2, monomers having structure 3 and mixtures thereof:



- 10 wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

52. The membrane electrode assembly of claim 51 wherein the compounds containing single or multiple vinyl groups are divinyl benzene or triallyl cyanurate.

- 15 53. The membrane electrode assembly of claim 51 wherein the substituents X on co-monomer of structure 3 are selected from the group consisting of hydrogen, halogen; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; and a perfluoroalkyl group containing oxygen, chlorine or bromine, wherein the
20 perfluoroalkyl group comprises C1 to C10 carbon atoms.

54. The membrane electrode assembly of claim 41 wherein the base polymer is a homopolymer or copolymer of non-fluorinated, fluorinated, and perfluorinated monomers.

- 25 55. The membrane electrode assembly of claim 54 wherein the base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene), poly(ethylene-chlorotrifluoroethylene), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoroalkyl vinyl ether), poly(tetrafluoroethylene-perfluoromethyl vinyl ether), poly(tetrafluoroethylene-perfluoropropyl vinyl ether),

polytetrafluoroethylene, modified polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, poly(vinylidene fluoride-hexafluoropropylene), polyethylene, and polypropylene.

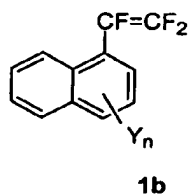
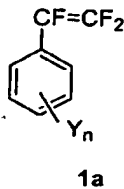
56. The membrane electrode assembly of claim 54 wherein the
5 base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene), poly(ethylene-tetrafluoroethylene-termonomer), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluorovinylether), polytetrafluoroethylene, poly(ethylene-chlorotrifluoroethylene); poly(vinylidene fluoride), and
10 poly(vinylidenefluoride-hexafluoropropylene).

57. The membrane electrode assembly of claim 56 wherein the base polymer comprises a terpolymer of ethylene, tetrafluoroethylene (TFE), and 1 to 10 mole% of a perfluorobutyl ethylene.

58. The fluorinated ion exchange polymer of claim 55 wherein the
15 perfluoro(alkyl vinyl ether), is perfluoro(propyl vinyl ether) or perfluoro(ethyl vinyl ether).

59. The membrane electrode assembly of claim 54 wherein the base polymer comprises a terpolymer of ethylene, tetrafluoroethylene (TFE), and 1 to 10 mole% of a termonomer such as perfluorobutyl
20 ethylene.

60. An electrochemical cell comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises a
25 fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure 1a, structure 1b and mixtures thereof,



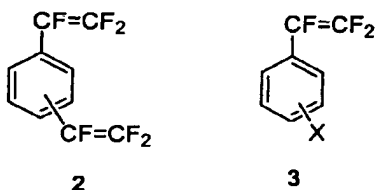
wherein Y is $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), or $-R_FSO_2N(M)SO_2R_F^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and

n is between 1 and 2 for **1a**, or n is between 1 and 3 for **1b**.

61. The electrochemical cell of claim 56 wherein the electrochemical cell is a fuel cell.

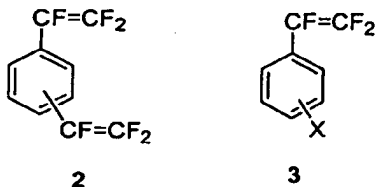
62. The electrochemical cell of claim 61 wherein the base polymer is in film form.

63. The electrochemical cell of claim 60 wherein the grafting monomers further comprise co-monomers selected from compounds containing single or multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, or monomers having the structure **2** or **3**



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

64. The electrochemical cell of claim 61 wherein the grafting monomers further comprise co-monomers selected from compounds containing single or multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, or monomers having the structure **2** or **3**



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

65. The fuel cell of claim 61 further comprising at least one electrode prepared from an electrocatalyst containing composition present on the first and second surfaces of the polymer electrolyte membrane.

5 66. The fuel cell of claim 60 further comprising at least one gas diffusion backing.

67. The fuel cell of claim 61 further comprising a gas diffusion electrode present on the first and second surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition.

10 68. The fuel cell of claim 61 further comprising a means for delivering a fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, hydrogen or methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode.

15 69. The fuel cell of claim 64 further comprising a means for delivering a fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, hydrogen or methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode.

20 70. The fuel cell of claim 68 wherein the fuel is an alcohol or ether.

71. The fuel cell of claim 70 wherein the fuel is methanol.

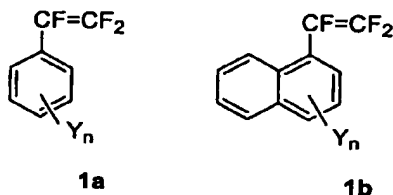
72. The fuel cell of claim 68 wherein the fuel is hydrogen.

TITLE

TRIFLUOROSTYRENE CONTAINING COMPOUNDS GRAFTED TO
BASE POLYMERS, AND THEIR USE AS POLYMER ELECTROLYTE
MEMBRANES

ABSTRACT OF THE DISCLOSURE

A fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure 1a, structure 1b and mixtures thereof,



wherein Y is selected from the group consisting of $-R_FSO_2F$ (sulfonyl fluoride), $-R_FSO_3M$ (fluorosulfonic acid or salt), $-R_FSO_2NH_2$ (fluorosulfonamide), and $-R_FSO_2N(M)SO_2R_F^2$ (imide); wherein M is H, an alkali cation, or ammonium; and R_F and R_F^2 groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and n is between 1 and 2 for 1a, or n is between 1 and 3 for 1b. These ion exchange polymers are useful in preparing catalyst coated membranes and membrane electrode assemblies used in fuel cells.

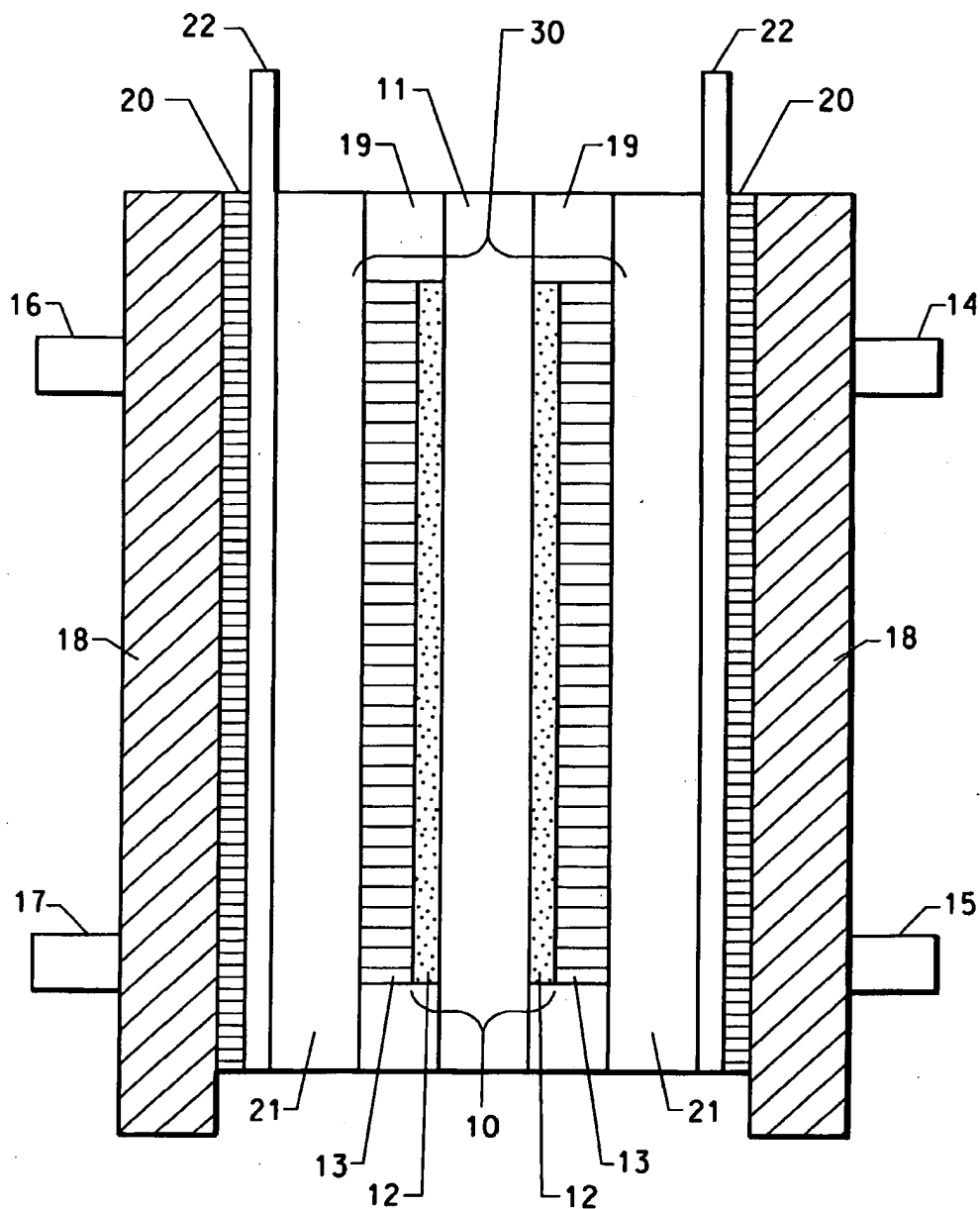


FIG. 1

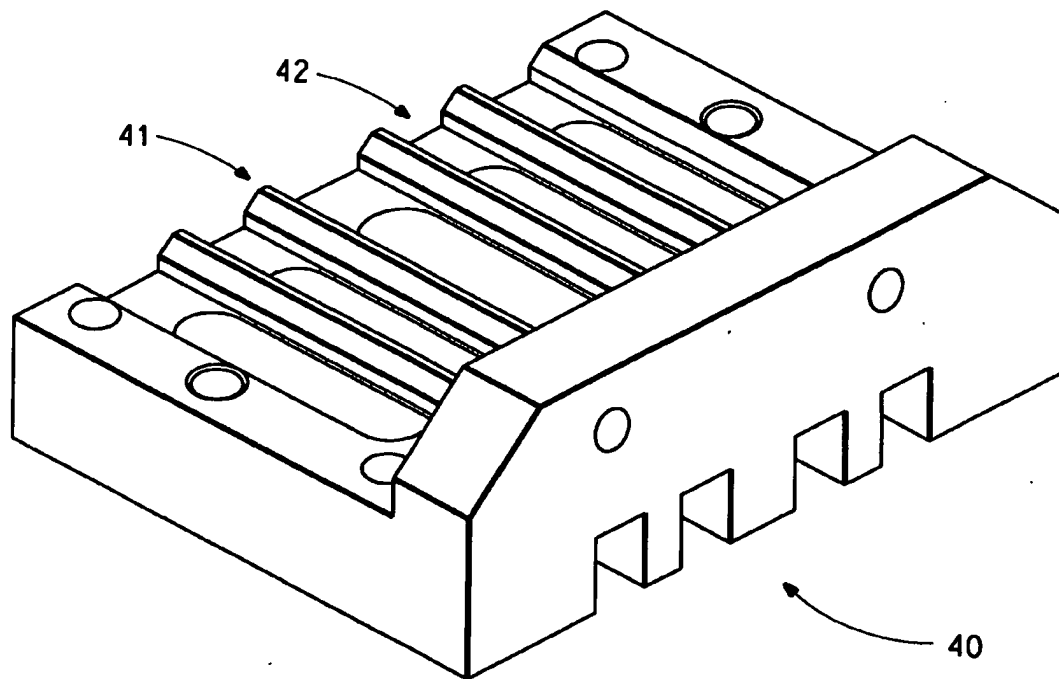


FIG. 2